A STUDY OF THE CHANGES IN THE IONIC AND COMPLEX-BOUND SULFATE OF CHROME LEATHER BY RADIOISOTOPE TECHNIQUES*

ABSTRACT

In chrome leather, sulfate and other anions may be present either electrostatically bound to positively charged groups or coordinately bound in the chromium complex. The amounts bound n these two ways may alter during storage of leather, and an attempt has been made to follow such changes by a radioisotope method.

The exchange of sulfate ions in chrome leather with sulfate in solution has been followed using isotopically labelled sulfate. Three rates of exchange have been distinguished: the first, probably instantaneous and presumably representing ionically bound sulfate; the second, essentially complete in about a day; and the third, a much slower exchange continuing over periods of 30 to 40 days.

The presence of two phases and the difficulties of maintaining equilibrium with respect to pH and distribution of sulfate, other than $^{35}SO_4$, in the system make it impossible to derive anything other than a rough estimate of the proportions of sulfate exchanging at the three rates. The results suggest that up to one mole of sulfate is coordinately bound for every atom of chromium present in the leather.

Pyrogallol causes little displacement of sulfate from chrome leather. Mimosa extract releases ionically bound sulfate by reason of the simple acid anions which it contains; displacement of coordinately bound sulfate follows slowly at about the same rate as the exchange of sulfate with itself.

400 ml. chromic sulfate liquor (3% Cr_2O_3 on skin weight) as above. To one of the tanning solutions ^{35}S-labelled sodium sulfate was added, and the solution was boiled before use.

Experiment III.—One hundred grams of oxhide was tanned as above, using 600 ml. chromic sulfate (6% Cr_2O_3 on skin weight) which had previously been boiled with labelled sodium sulfate.

Analyses of the leathers are given in Table I.

TABLE I

COMPOSITION OF LEATHERS

		Experiment I		Experiment II		Experiment III
		Active	Inactive	Active	Inactive	Active
Moisture—g. per 100 g. air-dry leather		16.3	16.4	18.8	21.2	—
Cr_2O_3—g.	per 100 g.	3.89	3.36	3.24	3.65	1.28
Cr—mmoles	moisture-free	51.2	44.2	42.6	48.0	16.9
SO_4—mmoles	leather	73.9	56.1	67.6	78.5	32.2

Measurement of exchange—Leather containing labelled sulfate was placed in an inactive solution, or vice versa, and aliquots were removed after various intervals for precipitation of the sulfate with barium chloride (4). Counts were made on infinitely thick samples using a thin end window Geiger Tube and an Isotope Developments Ltd. Scaler (Model 500 B). All results are expressed as counts per minute and corrected for decay.

Counts at infinite thickness are proportional to the specific activity of the sulfate and hence can be used as a measure of exchange. At equilibrium exchange the labelled sodium sulfate will be evenly distributed throughout the total sulfate in the system, and the specific activity in the two phases will be the same.

In Experiment I half the sample (5 g.) of the active leather was transferred to 40 ml. of the inactive tanning solution and vice versa. In this way it was hoped to have two identical systems except for the difference in the location of the active sulfate. Samples (1 ml.) were taken at intervals for precipitation.

In Experiment II, 10 g. leather was placed in 100 ml. solution containing the same amount of sulfate as that present in the leather, and 2-ml. aliquots were taken for precipitation. Both these experiments were carried out at room temperature, approximately 20°C.

INTRODUCTION

It is known that chromium salts in solution undergo slow changes, such as olation, resulting in the formation of complexes containing two or more chromium atoms and that the interaction between chromium and complexing organic ligands takes many hours to reach equilibrium. It seems probable that similar changes also occur in the chromium complexes present in leather, provided sufficient moisture is present, and probably account for the decrease in pH and slight increase in shrinkage temperature observed on storage over water at 40°C. Various suggestions have also been made regarding loss of sulfate from the chromium complex on drying and heating.

Sulfate will be present in the leather either electrostatically bound to positively charged basic groups of the protein or to the chromium complex and also bound in the complex by one or two coordinate valencies (1). The amount of ionic sulfate present will be dependent on the pH, the amount of chromium fixed, and the extent of washing.

The uptake of chromium will increase the net positive charge on the protein both by reacting with negatively charged carboxyl groups and by the introduction of a positively charged chromium complex. By analogy with modified proteins (2, 3) it may be expected that ionic sulfate equivalent to this excess positive charge will be difficult to remove, and it seems doubtful if neutralization to pH 5 or treatment with pyridine as has been suggested does in fact remove all such sulfate (1).

An attempt has, therefore, been made to obtain further information on the ways in which the sulfate is held in leather and on the changes which occur on heating and storage, using radioisotope exchange methods. The possibility of determining the relative effects of tans in displacing sulfate from the chromium complex was also examined. The results were somewhat inconclusive and afford a good illustration of the difficulties involved in the interpretation of such experiments, particularly with chromium salts which undergo slow changes and with which equilibrium conditions are not readily attained.

EXPERIMENTAL

Raw Material—Commercial pickled and degreased Cape-type sheepskin or limed oxhide (middle split) were cut into pieces about 1 mm. square and tanned as indicated below.

Experiment I.—Ten grams of sheepskin was tanned in 20 ml. basic chromic sulfate liquor (2% Cr_2O_3) and 60 ml. water, with or without the addition of a small amount of S^{35}-labelled sodium sulfate. Solutions were made basic with sodium bicarbonate to pH 3.9, and the tanned pieces were washed in tap water and acetone-dehydrated.

Experiment II.—2 x 60 g. sheepskins were pickled to pH 3.0 in 2% sodium sulfate with the addition of sulfuric acid, washed, and tanned for 72 hours in

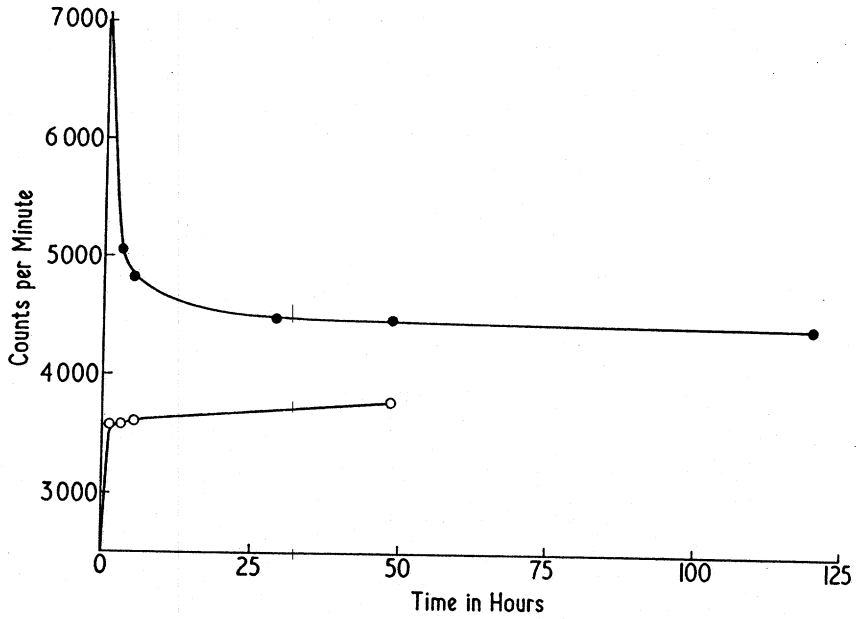

FIGURE I.—Exchange of labelled sulfate between leather and solution—Experiment I.
● —— ● Active solution.
○ —— ○ Active leather.

these become more pronounced if the curves are plotted on an extended time scale (*see* Fig. 4—broken lines).

The first experiment was arranged to give two similar systems differing only in the initial location of the labelled sulfate. Thus, the counts at equilibrium should be the same in both systems, and in theory, the two curves in Fig. 1 should meet at this point, making it possible to estimate an approximate time for complete exchange. Unfortunately, owing to the difficulties of obtaining reproducible results with chromium solutions, these conditions were not attained, the sulfate content of the active leather being appreciably greater than that of the inactive and that of the active solution being correspondingly less than that of the inactive. The results, however, indicate that 10 days or more are required for equilibrium to be approached and that about 70–75% of the sulfate in these leathers exchanged very rapidly and is, therefore, presumably ionically bound.

It is theoretically possible to calculate the equilibrium value for the counts at infinite thickness provided the concentration of sulfate in the two phases C_1 and C_2 and the "total number" of counts, χ, initially present in the system are known. At equilibrium the counts will be distributed between the two phases in accordance with the concentrations of sulfate and the specific

In Experiment III it was found more convenient to set up separate samples for each time in order to avoid alterations in the ratio of solution to leather. Two grams of leather was placed in 10 ml. of each of the following solutions:

(*a*) 2.5% Na_2SO_4
(*b*) 10% mimosa extract
(4.8% tans; 3.3% nontans)
(*c*) 1% pyrogallol

The solutions were kept at 25 °C. for periods up to 30 days, and 5-ml. samples were taken for precipitation. In the case of the mimosa and pyrogallol, sodium sulfate was added before precipitation so that the dilution of active by inactive sulfate was the same in the three systems.

Analytical methods—Sulfate was precipitated with barium chloride (4). The sample was made 0.2*N* with respect to HCl and heated in a boiling water bath, and *N* $BaCl_2$ was added. When appreciable amounts of chromium were present 1 ml. *N* sodium acetate was added to reduce coprecipitation of chromium. After cooling, the precipitate was separated by centrifugation, washed twice with water and twice with methanol, and then made up into a slurry with about 0.4 ml. methanol. The slurry was transferred to a 2.5-cm.-diameter planchet and dried under an infrared lamp.

Total sulfate in the leather was determined by digestion of 1 g. samples in 10 ml. conc. HNO_3 and 10 ml. conc. HCl. The solution was boiled to remove any chlorine and evaporated to about 1 ml.; then 1 ml. *N* sodium acetate was added, and the sulfate was precipitated as above.

Chromium was determined by perchloric acid oxidation followed by titration with ferrous ammonium sulfate (5). Tans and nontans in the mimosa liquor were determined by S.L.T.C. Official Methods (6).

RESULTS

The results of the first two experiments are presented graphically in Figs. 1–4, in which counts per minute at infinite thickness are plotted against time. In all cases, whether starting with active leather or active solution, there was a rapid change in count rate over the first few hours, followed by a much slower exchange which continued over periods of 20 days or more.

The rapid change was affected by the rate of division of the leather and by agitation of the solution, and the rate of diffusion of the solution into the interstices of the leather is presumably an important factor governing the rate. Similar rapid changes in count rate were produced by the addition of any salt and by changes in pH, and the inference is that it is primarily due to exchange of ionic species. There is a suggestion of two inflexions in some of the curves, one after about 1–2 hours and the other after about 40 hours, and

counts observed in all three experiments does in fact represent exchange or whether it is due to slow displacement of sulfate from the complex by hydroxyl ions (olation) or by carboxyl groups of the protein. However, if only the two faster rates represent exchange, the equilibrium value of counts should be approached in a relatively short time (judging from the slope of the broken lines in Fig. 4, in 24 hours or less), and this is manifestly not so. It seems, therefore, that the slow change in count over the longer periods of time is primarily due to exchange. It is possible that it represents sulfate bound into the complex by two valencies.

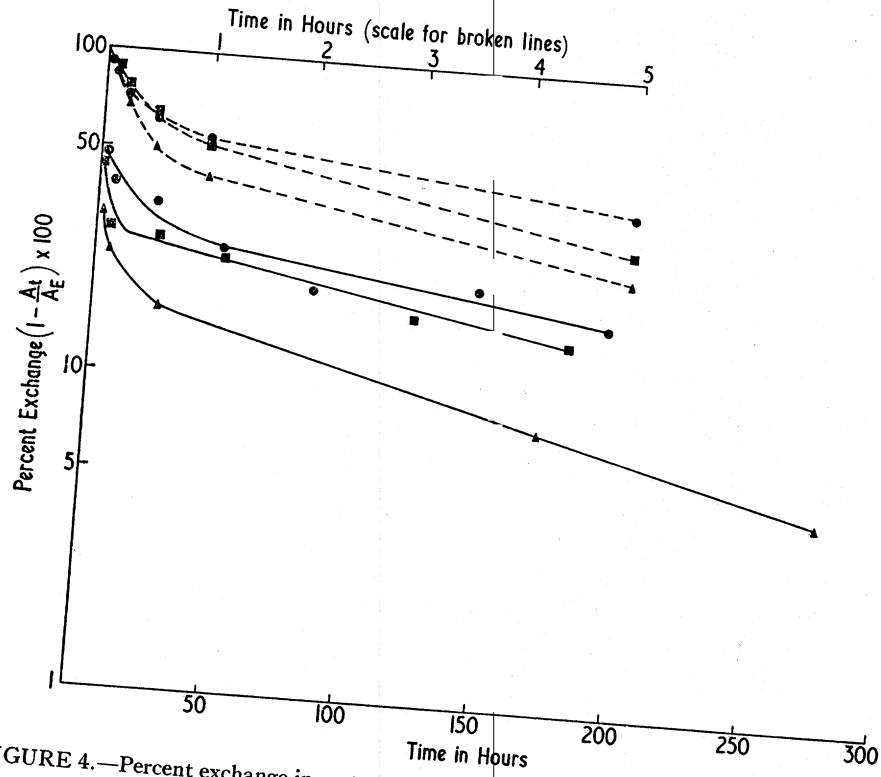

FIGURE 4.—Percent exchange in system active solution/inactive leather.—Experiment II.

● —— ● Untreated leather.
■ —— ■ Leather heated in boiling water for 10 min.
▲ —— ▲ Leather heated dry at 65°C. for 17 days.
Broken lines — extended time scale.

By extrapolation of the straight-line portions of the curves in Fig. 4 to zero time it is theoretically possible to obtain a rough estimate of the percentage of the total sulfate exchanging at the different rates (Table II). In view of the changes in pH, however, it is probable that the estimates for the sulfate exchanging at the slowest rate are too low.

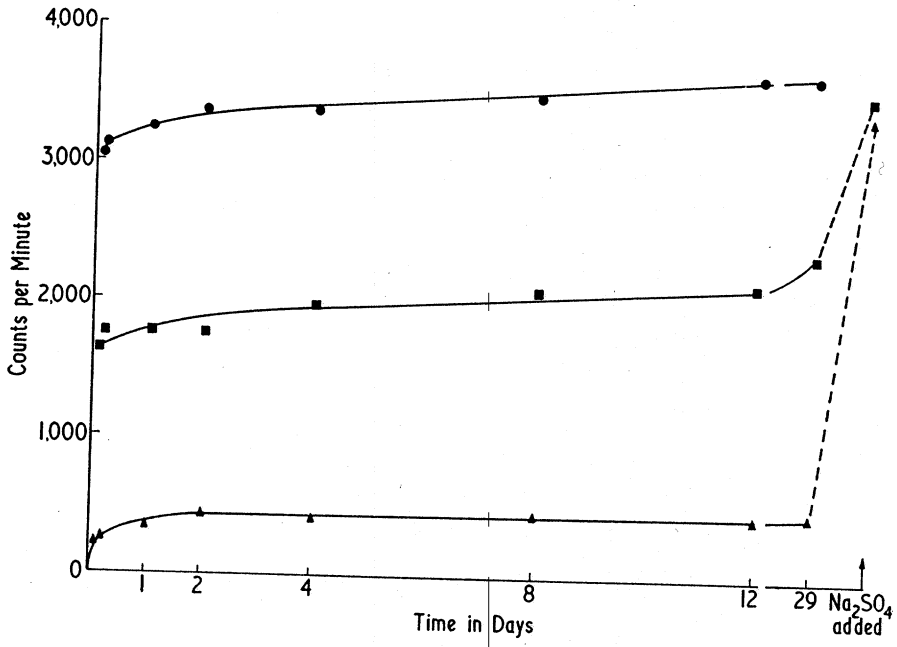

FIGURE 5.—Displacement of active sulfate from leather by sulfate, pyrogallol, and mimosa.

● —— ● Sulfate.
■ —— ■ Mimosa.
▲ —— ▲ Pyrogallol.
Broken lines — increase in counts on addition of sodium sulfate.

very slow rate. The concentration of pyrogallol was rather low, and further exchange may have been limited by reason of this. Again there was a fall in pH during the exchange, thus complicating interpretation.

Raising the temperature to 50°C. after 30 days did not speed up the exchange with any of the three materials, perhaps because it was essentially complete, but addition of sulfate to the pyrogallol and mimosa caused a rapid increase in counts to values approaching that of the sulfate, indicating displacement of any remaining ionic sulfate. The general inference is that pyrogallol at the concentrations used causes little, if any, displacement of ionic sulfate and only limited displacement of complex-bound sulfate. Mimosa extract removes about half the ionic sulfate, presumably by exchange of the anions in the nontan fraction, and subsequent slow displacement of sulfate from the complex proceeds at much the same rate as sulfate with sulfate. It is not possible to say how far this is due to the nontan acids and how far to the tan itself.